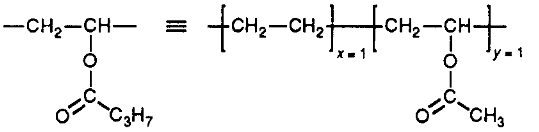
involving copolymers and herein lies a major conceptual difference between our approach and that of groups advocating the use of repulsion models for copolymer blends. We make no distinction between, for example, PVC blends with the "homopolymer" poly(vinyl *n*-butyrate) (PVBu) and its isomorphous equivalent, an average repeat of an equimolar EVA "copolymer".


PVBu

~EVA[75]

It could be argued that PVBu is a "copolymer" and an appropriate χ can be defined between the CH_2's in the side chain and the residual vinyl acetate unit. But instead of separating just the ethylene group in this manner, why not include the methyl and the main chain–CH_2–CH–groups? Where does one draw the line? Taking this process to the extreme, nearly all polymers can be considered "copolymers" (the only exceptions being polymethylene, polytetrafluoroethylene, and the like, and even these polymers can be reduced to different atomic contributions). For most miscible blends there is usually evidence for some favorable interaction, and we believe it is better to attempt to separate these from the unfavorable interactions embodied in an average nonassociated solubility parameter.

The miscibility behavior of PVC blends with EVA copolymers now follows in a straightforward manner. The homopolymers PVC and PVAc are miscible, but as the concentration of ethylene units in the EVA copolymer (or alternatively, in the homologous series of the homopolymers PVAc, PVPr, PVBu, etc.) is raised, the number of favorable interactions decreases. χ also changes, and at some critical concentration of ethylene units the homopolymer–copolymer blend becomes immiscible. In the more complex case of the poly(vinyl acetate-*co*-vinyl chloride) blends the polymer molecules strongly self-associate, and this must be balanced with the competing interactions that would form with CPVC. Furthermore, given the results presented here we would also anticipate strong $\Delta\chi$ affects in PVAc–CPVC blends.

Finally, it is important to note that specific interactions should be described by a free energy term, so that it is possible to have a positive enthalpy of mixing (as Cruz-Ramos and Paul[10] determined for PVC–PVAc model compounds), providing that this is compensated by a gain in entropy upon mixing. This is common in, for example, hydrogen-bonded systems where one of the components self-associates. As a result, more hydrogen bonds between like molecules can be broken upon mixing than are formed between unlike molecules. This can result in a large positive enthalpy of mixing that is more than compensated by a gain in "freedom" or entropy of the no longer associated molecules or segments.

Conclusions. 1. Under the appropriate experimental conditions a miscible blend of PVC and PVAc can be prepared from a solution of the polymers in MEK at room temperature.

2. PVC–PVAc blend samples prepared from THF solution were found to be grossly phase separated that apparently arises from a powerful $\Delta\chi$ effect.

3. PVC–EVA blends has been previously considered to represent one of the classic examples of a special class of blends where a homopolymer (PVC) is miscible with a range of copolymers of specific composition (EVA) but immiscible with both homopolymers (PE and PVAc) derived from the monomers used to synthesize the copolymer. The results presented here cast doubt on this assertion.

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Registry No. PVC, 9002-86-2; PVAc, 9003-20-7.

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Screening Effect on Viscoelasticity near the Gel Point

There has recently been many experimental investigations[1-14] of the static and dynamic properties of branched polymers near the gel point. The chief objective of these studies is to verify the theories of gelation and properties of polymers in the vicinity of the sol–gel transition. There are two theories of gelation. One is the classical theory of Flory,[15,16] Stockmayer,[17] and Zimm.[18] The other is the percolation theory.[19,20] Many researchers[1-10] have demonstrated clearly that the percolation theory is quite successful in predicting the static properties of branched polymers (such as distributions of size and mass of clusters, correlation length, and fractal dimension) near the gel point. However, the status is not so clear regarding the dynamical properties of branched polymers near the gelation threshold.

In a typical experiment, difunctional polymers or monomers are mixed with tri- or tetrafunctional molecules (cross-linking agents or star polymers) under suitable chemical conditions, and the cross-linking process is carried out for a certain duration. The extent of cross-linking is controlled by either "poisoning" the reaction at a known time of reaction or controlling the stoichiometry and running the reaction to completion. The samples obtained at different extents of the cross-linking reaction are then

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analyzed and their viscoelastic properties determined. In a typical rheological measurement, a sinusoidal strain wave of frequency ω is applied to the sample in conventional cone-and-plate or parallel plate rheometers, and the resulting stress is analyzed to determine the frequency dependencies of the storage (G') and loss (G'') moduli. Near the gel point both G' and G'' obey the common power law, $G' \sim G'' \sim \omega^n$ over a range of frequencies probing internal modes of the polymer. This implies that the relaxation modulus $G(t)$ decays with time t as $G(t) \sim t^{-n}$. Also, in this frequency regime the complex viscosity $\eta^*(\omega) \sim \omega^{n-1}$.

The determination of the exponent n has recently been of considerable theoretical interest.[5,9,11,19-22] Consider a polymer of fractal dimension d_f, which relates the molecular weight M of the polymer to its spatial size R as

$$R^{d_f} \approx M$$

When hydrodynamic and excluded-volume interactions are included and entanglement effects are ignored, n is derived for a *monodisperse* solution of polymers of fractal dimension d_f to be (see Table 1 of ref 21)

$$\begin{aligned} n &= d_f/d && \text{dilute} \\ n &= \tilde{d}_f/(\tilde{d}_f + 2) && \text{semidilute and unentangled dense} \end{aligned} \tag{1}$$

where d is the space dimension and $\tilde{d}_f$ is the fractal dimension of the polymer if the excluded-volume effect is fully screened. In deriving the above result for dense concentrations of the solution, the well-known effect[20,23] of screening of excluded-volume and hydrodynamic interactions has been fully accounted for. Also, since entanglements are ignored and hydrodynamics is screened, Rouse dynamics prevails and leads to the above result. In fact, $\tilde{d}_f$ is related to d_f, according to (see eq 4.8 of ref 21) the "Flory type" formula

$$\tilde{d}_f = \frac{2d_f}{d + 2 - 2d_f} \tag{2}$$

For a *polydisperse* solution of polymers of fractal dimension d_f, n is obtained (when Rouse modes dominate the dynamics) as[5,9,11,19,22]

$$n = \frac{d_f(\tau - 1)}{d_f + 2} \tag{3}$$

where τ is the scaling exponent describing the size distribution function $\phi(M,\epsilon)$ near the gel point

$$\phi(M,\epsilon) \approx M^{-(\tau-1)}f(M/M_{\mathrm{char}}) \tag{4}$$

Here $\phi(M,\epsilon)\,\mathrm{d}M$ is the weight fraction of monomers belonging to molecules with molecular weight between M and $M + \mathrm{d}M$, and $\epsilon = 1 - (p/p_c)$, where p is the extent of the reaction and p_c is the p value at the gel point. f is a cutoff function ($f(x) \sim 1$ for $x < 1$ and $f(x) \to 0$ for $x > 1$) and M_{char} is the molecular weight of the largest finite polymer which diverges at the gel point as

$$M_{\mathrm{char}} \approx \epsilon^{-1/\sigma}$$

The classical theory ($d = \infty$) gives ($d_f = 4$, $\tau = 5/2$, $\sigma = 1/2$)

$$n = 1 \tag{5}$$

which is independent of d. On the other hand, the percolation theory gives

$$n = d/(d_f + 2) \tag{6}$$

where the hyperscaling hypothesis (see eq 53 of ref 19)

$$\tau - 1 = d/d_f \tag{7}$$

has been assumed. Although this assumption fails for the realm of classical theory ($d = \infty$), it is found to be satisfactory for $d = 2$ and 3. For $d = 3$, it therefore follows from the percolation theory ($d_f = 5/2$, $\tau \simeq 2.2$, $\sigma \simeq 0.46$) that

$$n = 2/3 \tag{8}$$

By investigating the rheological properties of branched polymer formed by rather short strands, Durand et al.[5] have shown that $n = 0.70 \pm 0.02$, thus supporting the percolation theory. Through a series of papers,[2-5] these authors have also confirmed the values of other exponents predicted by percolation model. Additional support for the percolation theory has been provided by Martin et al.[9] and Rubinstein et al.[11] who obtained $n = 0.70 \pm 0.05$ and 0.69 ± 0.02, respectively. While these experimental results demonstrate the validity of percolation theory by observing the same universal value of n close to the predicted value of 2/3, Winter and co-workers[12-14] have reported different values of n for different systems. At low extent of cross-linking using stoichiometrically balanced four-functional cross-linker and relatively long (about 125 monomers, but below entanglement molecular weight) bifunctional poly(dimethylsiloxane), Chambon and Winter[12] observed that $G' < G''$. With increasing extent of reaction, the two moduli increased in value and became more similar as in the works of Durand et al.,[5] Martin et al.,[9] and Rubinstein et al.[11] However, when the reaction was continued, Chambon and Winter observed a critical extent of reaction when $G' = G''$. Beyond the critical extent of the reaction, $G' > G''$ over the entire frequency range. At the critical extent of reaction, n was observed to be 1/2. Further experiments[13,14] with change of stoichiometry showed that the value of n increased from 1/2 to 0.66 as cross-linker deficiency is increased. Values of n lower than 1/2 have also been reported.[24,25] Therefore, it is doubtful that the percolation result as described above correctly describes the reality of polymer gelation.

The discrepancy between the results of Winter et al.[12-14] and those of Durand et al.[5] and others[9,11] may be due to either inadequate approach to the gel point under the conditions involved in the latter experiments or some new additional effects arising from relatively longer strands used in the former experiments or both.

It is well-known[20,23] that the excluded-volume effect of a chain in dilute solution gets progressively screened to give the ideal dimension of the chain as the concentration is increased. The shrinkage of the size of the polymer (i.e., increase in d_f) with concentration increase is established even for branched polymers from neutron- and light-scattering studies[3,4,26] with different dilutions. Therefore, we expect such a screening of the excluded-volume effect in a system where gelation is taking place, especially when cross-links are joined by long strands. In fact, computer simulations[27] and numerical studies[28] of structures like star-burst polymers show that the effective fractal dimension of the cluster increases even beyond 3 as the number of generations of cluster growth is increased. In the reaction bath where gelation is taking place, a family of clusters is present and the situation near the gel point is not unlike a polymer melt as far as the screening of excluded volume is concerned. Therefore the exponent n is now given by

$$n = d/(\tilde{d}_f + 2) \tag{9}$$

where $\tilde{d}_f$ is the fractal dimension of the branched polymer with the excluded-volume effect screened out and is related to d_f by eq 2. The hyperscaling assumption of the per-

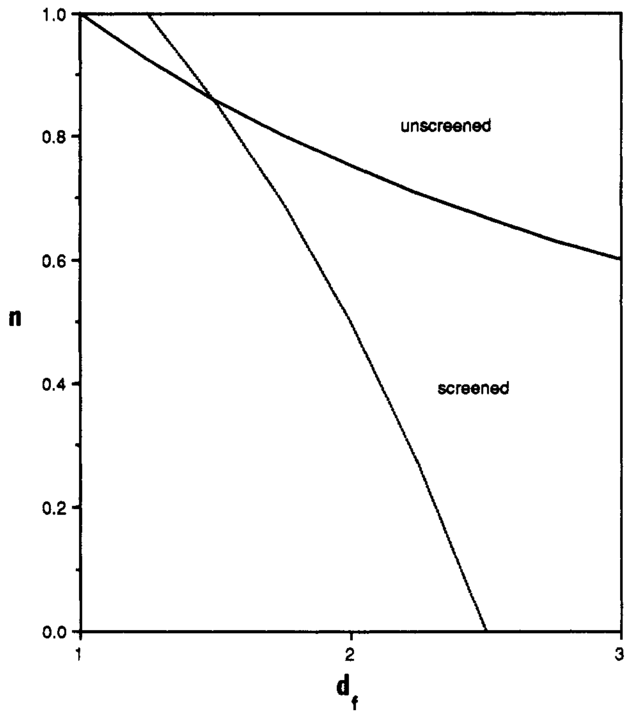

Figure 1. Dependence of n in $d = 3$ on d_f according to eq 6 and 10 for the unscreened and screened cases, respectively.

colation model, eq 7, has been used in writing down this equation. This assumption is valid for the conditions considered here. See ref 29 for more general cases. If only the two-body excluded-volume effect is of concern, $\bar{d}_f > d_f$. If there is only partial screening, then the dimension that appears in the denominator of eq 9 is some appropriate value between d_f and $\bar{d}_f$. Substituting eq 2 in eq 9 gives

$$n = \frac{d(d + 2 - 2d_f)}{2(d + 2 - d_f)} \qquad (10)$$

The dependence of n on d_f for both the unscreened and screened situations (eq 6 and 10, respectively) for $d = 3$ is given in Figure 1. These are to be taken as bounds and reality might lie between depending on the extent of screening. While n for the unscreened case changes from 1 to 2/3 as d_f changes from 1 to 5/2, n changes over the whole range of 0-1 in the same interval of d_f. It is to be noted that a small change in d_f around and above 2 can lead to a substantial change in $\bar{d}_f$ and consequently in the value of n. Specifically, $n = 1/2$ observed by Chambon and Winter corresponds to the situation[30] of $d_f = 2$; i.e., $\bar{d}_f = 4$ (the Zimm-Stockmayer dimension but combined with hyperscaling and not classical theory). The other values of n (in the range of 0.8-0.2) observed by Winter et al.[12-14,25] and Antonietti et al.[24] can be explained by a combination of percolation and either partial or full extent of screening depending on the nature of the particular chemical system.

In spite of the generality of the above-derived result, specific qualitative trends can be predicted. As the cross-linker deficiency is increased, the structure is more open than a fully cross-linked cluster and d_f is lower, leading to an increase in n for fixed extent of screening. If a collection of screened clusters is diluted with chains that are long enough screening is not affected any further and n is relatively insensitive to such dilutions. However, if dilution is performed with small molecular solvent, clusters will expand and n will increase. We finally conclude that the screening of excluded volume in clusters near the gel point can lead to significant changes in the scaling exponent characterizing the viscoelastic properties of such polymeric systems.

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Direct Formation of the Helical Polymer Conformation in Stereospecific Polymer Synthesis. X-ray Crystallographic Determination of Linear Chloral Oligomers[1]

We report the determination of the structure by X-ray single-crystal analysis of the linear oligomers of chloral (dimer to tetramer) that lead to the exclusively isotactic structure for polychloral.